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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/616,783	07/10/2003	Klaus Hohn	12406-006003	2003
26161	7590	05/04/2006	EXAMINER	
FISH & RICHARDSON PC P.O. BOX 1022 MINNEAPOLIS, MN 55440-1022			TRAN, MINH LOAN	
			ART UNIT	PAPER NUMBER
			2826	

DATE MAILED: 05/04/2006

Please find below and/or attached an Office communication concerning this application or proceeding.

**Office Action Summary**

Application No.

10/616,783

Applicant(s)

HOHN ET AL.

Examiner

Minh-Loan T. Tran

Art Unit

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-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 19 October 2005.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 17-40 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 17-40 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☒ The specification is objected to by the Examiner.
- 10) ☒ The drawing(s) filed on 7/10/03 is/are: a) ☐ accepted or b) ☒ objected to by the Examiner.
- Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☒ All b) ☐ Some \* c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
  2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
  3. ☒ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

\* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)  
Paper No(s)/Mail Date 3/27/06, 3/6/06, 12/5/05, 10/24/05, 10/19/05
- 4) ☐ Interview Summary (PTO-413)  
Paper No(s)/Mail Date. \_\_\_\_\_
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☒ Other: Attachment (4 pages)

## **DETAILED ACTION**

### ***Continued Examination Under 37 CFR 1.114***

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after allowance or after an Office action under *Ex Parte Quayle*, 25 USPQ 74, 453 O.G. 213 (Comm'r Pat. 1935). Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, prosecution in this application has been reopened pursuant to 37 CFR 1.114. Applicant's submission filed on 10/19/2005 has been entered.

### ***Information Disclosure Statement***

2. The information disclosure statements filed 10/19/05, 10/24/05, 12/05/05, 03/06/06, 03/27/06 have been considered.

### ***Drawings***

3. The drawings are objected to under 37 CFR 1.83(a). The drawings must show every feature of the invention specified in the claims. Therefore, the luminous substance pigments are substantially spherical particles as recited in claims 18, 29 or flakelike particles as recited in claims 19, 30 must be shown or the feature(s) canceled from the claim(s). No new matter should be entered.

Corrected drawing sheets in compliance with 37 CFR 1.121(d) are required in reply to the Office action to avoid abandonment of the application. Any amended replacement drawing sheet should include all of the figures appearing on the immediate

prior version of the sheet, even if only one figure is being amended. The figure or figure number of an amended drawing should not be labeled as "amended." If a drawing figure is to be canceled, the appropriate figure must be removed from the replacement sheet, and where necessary, the remaining figures must be renumbered and appropriate changes made to the brief description of the several views of the drawings for consistency. Additional replacement sheets may be necessary to show the renumbering of the remaining figures. Each drawing sheet submitted after the filing date of an application must be labeled in the top margin as either "Replacement Sheet" or "New Sheet" pursuant to 37 CFR 1.121(d). If the changes are not accepted by the examiner, the applicant will be notified and informed of any required corrective action in the next Office action. The objection to the drawings will not be held in abeyance.

### ***Claim Rejections - 35 USC § 112***

4. The following is a quotation of the first paragraph of 35 U.S.C. 112:

The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claims 17-40 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention.

The specification does not disclose the definition of the "mean grain diameter  $d_{50}$ " as recited in claims 17 and 28. Note that in the IDS filed on 10/19/2005, Applicants defined the "mean grain diameter  $d_{50}$ " is the median particle diameter based on a number-distribution (i.e., half of the particles have a diameter greater than or equal to this diameter and the other half of the particles have a diameter less than or equal to this number.)

The specification does not disclose the luminous substance pigments having grain sizes  $\leq 20 \mu\text{m}$  and a mean grain diameter  $d_{50} \leq 5 \mu\text{m}$  as recited in claims 17 and 28. Note that the luminous substance pigments having grain sizes  $\leq 20 \mu\text{m}$  and a mean grain diameter  $d_{50} \leq 5 \mu\text{m}$  are disclosed only in the Summary of the invention, but not in the Description of the preferred embodiment.

The specification does not disclose the iron content in the casting composition is  $\leq 20$  ppm. Note that page 8 of the Summary of the invention only discloses the iron content in the casting composition is  $\leq 5$  ppm and the iron content in the casting composition  $< 20$  ppm are advantageous.

The specification does not disclose the mean grain diameter  $d_{50}$  of the luminous substance pigments is between 1 and 2 micrometers as recited in claims 20 and 31. Note that the mean grain diameter  $d_{50}$  of the luminous substance pigments is between 1 and 2 micrometers is disclosed only in the Summary of the invention, but not in the Description of the preferred embodiment.

5. The following is a quotation of the second paragraph of 35 U.S.C. 112:

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The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 17-40 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

In claim 17, lines 10 and 11, "mean grain diameter  $d_{50}$ " is unclear as to whether it is being referred to the mathematical average value of the grain diameter.

In claim 28, lines 8 and 9, "mean grain diameter  $d_{50}$ " is unclear as to whether it is being referred to the mathematical average value of the grain diameter.

### ***Claim Rejections - 35 USC § 103***

6. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 17-40 are rejected under 35 U.S.C. 103(a) as being unpatentable over Shimizu et al. (5,998,925) in view of Phosphor Handbook, Dec 1987 (English version.)

With regard to claims 17, 20, 21, 22, 31 and 28, figure 1 of Shimizu et al. disclose a light emitting semiconductor body 102 for use in an LED housing 100; the semiconductor body 102 being provided with a layer comprising a wavelength-converting casting composition 101; the casting composition 101 comprising luminous substance particles; the luminous substance particles comprising luminous substance pigments selected from the group consisting of garnet fluorescent doped with cerium

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(rare earth), aluminates doped with cerium (rare earth.) Note lines 64-67 in column 9, lines 1-35 in column 10 of Shimizu et al.

Shimizu et al. does not disclose the luminous substance pigments having grain sizes  $\leq 20 \mu\text{m}$  and a mean grain diameter  $\leq 5 \mu\text{m}$ . However, page 275 of Phosphor Handbook discloses the YAG:Ce phosphor particles having grain sizes  $\leq 20 \mu\text{m}$  (because particles having grain sizes greater than  $3 \mu\text{m}$  are removed, 2<sup>nd</sup> paragraph in the right hand column of page 275) and a mean grain diameter about 4-5  $\mu\text{m}$  or less (1<sup>st</sup> paragraph in the right hand column of page 275.) is well known phosphor. Therefore, it would have been obvious to one of ordinary skill in the art to use the phosphor particles having grain sizes  $\leq 20 \mu\text{m}$  and a mean grain diameter  $\leq 5 \mu\text{m}$  such as taught by the Phosphor Handbook in the casting composition of Shimizu et al. in order to enhance the color of the emitted light.

With regard to claims 18, 19, 29, 30, figure 1 of Shimizu et al. does not disclose the luminous substance pigments are substantially spherical particles or flakelike particles. However, the Phosphor Handbook (see attachment- Chapter 2 : Powder Properties) discloses the luminous substance pigments having plurality of shapes such as spherical particles or flakelike particles (right hand column.) Therefore, it would have been obvious to one of ordinary skill in the art to use the luminous substance pigments having spherical particles or flakelike particles such as taught by the Phosphor Handbook in the casting composition of Shimizu et al. because such luminous substance pigment shapes are well known in the art for forming phosphor. Further, although Shimizu et al. does not teach exact the shape of the luminous substance

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pigments as that claimed by Applicant, the shape differences are considered obvious design choices and are not patentable unless unobvious or unexpected results are obtained from these changes. It appears that these changes produce no functional differences and therefore would have been obvious. Note *In re Leshin*, 125 USPQ 416, *In re Woodruff*, 919 F.2d 1575, 1578, 16 USPQ2d 1934, 1936 (Fed. Circ. 1990).

With regard to claims 23 and 32, figure 1 of Shimizu et al. does not disclose an iron content in the casting composition is  $\leq 20$  ppm. However, it would have been obvious to one of ordinary skill in the art to form the casting composition of Shimizu et al. having an iron content is  $\leq 20$  ppm in order to prevent the reducing in powder brightness. Note page 172 (right hand column) of the Phosphor Handbook is cited to support for the well known position.

With regard to claims 24 and 33, lines 54-59 in column 16 of Shimizu et al. disclose the luminous substance pigments are provided with a silicon coating 101.

With regard to claims 25, 27, 34 and 36, lines 30-38 in column 9, lines 41-58 in column 14 of Shimizu et al. disclose the luminous substance pigments (i.e. phosphor) convert the blue radiation having maximum luminescence intensity at a wavelength between 420 nm and 460 nm that is emitted from the semiconductor body 102 into light with longer wavelength (white light).

With regard to claims 26 and 35, lines 60-62 in column 16 of Shimizu et al. disclose the layer comprising a wavelength-converting casting composition 101 containing light-scattering particles such as silicon dioxide, titanium oxide.



With regard to claims 37-40, figure 1 and lines 54-59 in column 16 of Shimizu et al. disclose the casting composition 101 comprises a transparent material such as epoxy resin.

***Conclusion***

7. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Minh-Loan T. Tran whose telephone number is (571) 272-1922. The examiner can normally be reached on Monday-Friday 9:00 AM-5:30 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Nathan J. Flynn can be reached on (571) 272-1915. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Mlt  
04/2006

  
Minh-Loan T. Tran  
Primary Examiner  
Art Unit 2826

# Attachment

## Chapter 2: Powder Properties

The characteristics of powders appear in all physical properties, and there are unique techniques for measuring each. The physical properties of powders vary depending on their state — dry powder, compression-molded powder, sintered compacts, or damp powder or a dispersed system such as a slurry — and the devices and operations for measuring them vary as well. Items that might be termed powder physical properties would be (1) the graininess of the powder particles (particle size and shape), (2) the packing and flow properties of the powder particles (the aggregate state and fluid state depending on their graininess and dynamic properties, called powder physical properties in the narrow sense), and (3) the electrical, magnetic, optical, and acoustic properties determined by the powder's characteristic electrical conduction phenomena, scattering phenomena, surface phenomena, etc. (called physical properties in the broad sense). In this chapter we cover phosphors, so optical properties will be discussed in other chapters (IV chapter 2 and V chapter 1), and our discussion of the other physical properties, which are considered not directly relevant, will be limited to (1) and (2). For (3), see references 1) and 6) to 8) at the end of the chapter.

### 2.1 Particle size terminology and measurement

#### [1] Particle shape and size

If particles all had a spherical or cubic shape, their size could be indicated by their diameter or by the length of an edge, but such phosphor powders are extremely rare. Even with a powder that consists of a collection of particles of irregular shape, if it is a collection of particles that are nearly similar statistically, one can note either the length (l), breadth (b), or height (h), or make size comparisons by a mean diameter or equivalent diameter listed in Table 4.2.1.

Table 4.2.1: Mean and equivalent diameters of a particle

Term	Defining formula
Two-axis mean diameter	$(l+b)/2$
Three-axis mean diameter	$(l+b+h)/3$
Harmonic mean diameter	$3(1/l+1/b+1/h)^{-1}$
Enveloping rectangle equivalent diameter	$(bl)^{1/2}$
Square equivalent diameter	$(l)^{1/2}$
Circle equivalent diameter	$(f/\pi)^{1/2}$
Cuboid equivalent diameter	$(lbh)^{1/3}$
Cylinder equivalent diameter	$(fh)^{1/3}$
Cube equivalent diameter	$(V)^{1/3}$
Sphere equivalent diameter	$(6V/\pi)^{1/3}$

l: length, b: breadth, h: height, f: projected area, V: volume

(a) **Circularity and sphericity** The shape of a particle is frequently described by the ideal shape that is closest to it, such as a sphere, cube; column, needle, flake (thin sheet), lump, etc. But when the shape of the particles has a very important meaning, we may want to express the shape numerically. For this purpose, there are ways to express circularity, sphericity, etc. to indicate how similar the particles are to ideal spherical particles.

Circumference of a circle whose area equals the projected area of a particle

Circularity =  $\frac{\text{Circumference of a circle whose area equals the projected area of a particle}}{\text{Perimeter of the projection of a particle}}$

Perimeter of the projection of a particle

Surface area of a sphere of the same volume as a particle

Sphericity =  $\frac{\text{Surface area of a sphere of the same volume as a particle}}{\text{Surface area of a particle}}$

Surface area of a particle

With particles of irregular shape, it is sometimes difficult to measure the perimeter or surface area, and what is sometimes used according to the following definition is

Practical sphericity =  $\frac{\text{Volume of a particle}}{\text{Volume of a circumscribing sphere}}^{1/3}$

(b) Shape factor, effective diameter, and equivalent diameter

Many of the methods for measuring particle size make use of physical measurement that assumes a particle of spherical or other simple shape. The coefficient applied in such a case that indicates the relationship between a representative diameter (if a sphere, its diameter)  $D_p$  and the particle size of the particle of interest is called a shape factor, and usually what are used for an actual collection of particles are the volume shape factor  $\phi_v$  and the area shape factor  $\phi_s$ , which are computed by the following equations from measurements of the mean volume  $V$  and the mean surface area  $S$  per particle.

$$V = \phi_v D_p^3 \quad (4.2.1)$$

$$S = \phi_s D_p^2 \quad (4.2.2)$$

For a spherical particle,  $\phi_v = \pi/6$ , and  $\phi_s = \pi$ . The value of these factors, it should be noted, depends on the laws of physics as they apply to taking measurements. Applying the laws of physics for measurement methods, from the measured values, the phenomenon being measured is sometimes indicated by the particle diameter of particles of ideal shape (for example, spherical shape) that would have the same effect. This is called the effective diameter. In precipitation in a liquid, the diameter of a spherical particle of the same density that precipitates at the same rate is the effective diameter, and because the Stokes equation is used, this is called the Stokes diameter.

As another method in which a shape factor is not used, there is the method of expressing it as the diameter of a particle of ideal shape that can be compared with the size of the particle; this is called the equivalent diameter, and typical examples are listed in Table 4.2.1.

## [2] Particle size distribution

Particle diameter is a quantity that indicates the size of each particle when applied to individual particles such as those listed as examples in Table 4.2.1, and particle size is a concept that tries to express as an average the size of the particles in a collection of particles that form a powder. An actual powder is always

a collection of particles that has a distribution in sizes.

### (a) Types of particle size distribution

With regard to a general distribution, there are two types, a frequency distribution and an accumulated distribution, but apart from this classification, there are the following types of particle size distributions. In describing a frequency distribution, the distribution of particles included in particle diameter classes (the range of  $D_n$  and  $D_{n+1}$ ) is expressed in the following ways.

- (1) Number-based distribution: How many particles among the total number of particles  $\Sigma n$
- (2) Length-based distribution: How much length among the total  $\Sigma nD$  of the diameters of all the particles
- (3) Area-based distribution: How much area among the total surface area  $\Sigma nD^2$  of all the particles
- (4) Weight-based distribution: How much weight among the total weight  $\Sigma nD^3$  of all the particles

The same sample has a different distribution mean, that is, a different value for the particle size, depending on which quantity the particle size distribution is based on. Theoretically, distribution (1) can be used, but the particle sizes that are relevant to the properties of actual powders are often those that are according to distributions (3) and (4).

### (b) Mean particle diameter

If the nature that indicates a powder is taken to be expressed by a nature indicated by a collection of particles of a given particle diameter  $D'$  that represents the distribution, then  $D'$  is called the mean particle size. Among the several mean diameters calculated from the distribution, what is taken as the mean particle size is often the mean particle diameter that is most suited for the above function. These are listed in Table 4.2.2. In this table,  $L$  is  $nD$ ,  $S$  is  $nD^2$ , and  $W$  is  $nD^3$ . Figure 4.2.1 shows graphs in which a given number-based distribution is expressed in terms of length-based distribution, area-based distribution, and weight-based distribution, along with ones by which the mean particle diameter from  $D_1$  to  $D_4$  is determined.

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## [3] Phosphors for flying spot tubes

Flying spot tubes are well known devices, have been used for transmitting pictures since the early days of the development of television technology, and because of their nature as a special application, we discuss them in this section. The luminescent spot on a picture tube is taken as the scanning light source and is focused onto the film by an optical system, and the changes in the amount of light that shines through according to the shading of the film is output as a video signal by a photoelectric cell. A fluorescent screen for this purpose requires high brightness, high resolution, short-duration persistence, and uniformity of brightness. And of course it must match the spectral sensitivity of the photoelectric cell. As phosphors,  $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Ce}^{3+}$  (P16) was once used for monochrome film and  $\text{ZnO}:\text{Zn}$  (P24) for color film, but both present the disadvantage of having low optical output and being prone to degradation. Each of the phosphors listed below is better in this respect and has superior properties.

- (a)  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (P46): luminescent peak wavelength 530 nm, 10% persistence time 150 ns.
- (b)  $\text{Y}_2\text{SiO}_5:\text{Ce}^{3+}$  (P47): luminescent peak wavelength 400 nm, 10% persistence time 70 ns.
- (c) {P46 (70%) + P47 (30%)} (P48): luminescent peak wavelengths 400, 525 nm, 10% persistence time 120 ns.
- (d)  $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$  (PYG): luminescent peak wavelength 515 nm, 10% persistence time 120 ns.

Among these, because of the requirement that a phosphor for color film have a broad emission spectrum, P48 was created by mixing two phosphors, but when phosphor particles whose particle surface electrochemical properties are different are mixed together, slight aggregation tends to occur due to the coating conditions, and this creates noise. On this point, the  $\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$  (PYG) of (d) has a unitary, broad emission spectrum as shown in Figure 3.3.65, including also the necessary blue region of the spectrum, and can be said to be well adapted to this purpose.

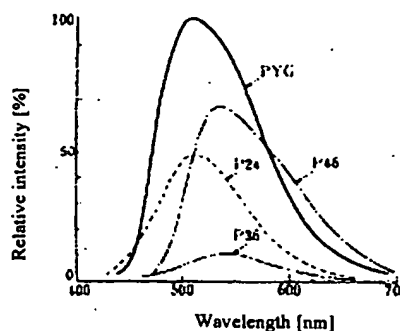


Figure 3.3.65: Emission spectra of color flying spot tubes [comparison under the same conditions]

$\text{Y}_3(\text{Al,Ga})_5\text{O}_{12}:\text{Ce}^{3+}$  is obtained by adding 2.94 moles  $\text{Y}_2\text{O}_3$ , 2.3 moles  $\text{Al}_2\text{O}_3$ , 2.7 moles  $\text{Ga}_2\text{O}_3$ , and 0.06 moles Ce in the form of cerium oxalate, mixing them with a ball mill, and baking in air at  $1,550^\circ\text{C}$ . Of course, care must be taken with the purity of the raw materials that are used, but an appropriate selection is made with regard to the particle size as well, and the particle diameter of the phosphor that is ultimately obtained is set to a mean value of 4-5  $\mu\text{m}$  or less.

The fluorescent screen is made by the precipitation method, but because brightness unevenness caused by tiny irregularities in the fluorescent screen creates a noise signal, the phosphor is sifted with a water sieve to remove particles greater than 3  $\mu\text{m}$ . One can use an ordinary binder like potassium silicate and an ordinary electrolyte like barium acetate, but care is required concerning their concentration and dispersion time in order to obtain good dispersability.

The frequency response of a color flying spot tube is shown in Figure 3.3.66. For a fluorescent screen that employs PYG it is 80% or more even in the high-frequency region of 1 MHz, and even in a lifetime test lasting 3000 continuous hours under the excitation conditions of an acceleration voltage of 20 kV and a current density of  $2 \mu\text{A}/\text{cm}^2$ , it maintains 90% or more of its luminescent output. Its color component ratios were measured using V-V 45, V-G 55,

### [5] Impurities and additives

The presence of specified impurities in phosphor raw materials can greatly reduce the luminous efficiency. Conversely, a small quantity of additives can have desirable effects, such as improving efficiency or reducing degradation. The type and quantity of impurities that affect properties vary greatly from one phosphor to another. In the following we present a number of examples.

It has long been known that the luminescence efficiency of zinc sulfide phosphor decreases considerably if a minute quantity of iron-family ions is present in it. An impurity that has this effect is called a killer. In looking at how the luminous intensity changes when  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  are added to  $\text{ZnS}:\text{Cu}$ , Al, we find that  $\text{Ni}^{2+}$  has the greatest effect: adding  $10^{-6}$  gram-atoms per mole of  $\text{ZnS}$  (about 0.6 ppm) already reduces the brightness by 30%, and at  $10^{-3}$  gram-atoms (about 600 ppm), no luminescence is seen at all anymore<sup>20)</sup> (see II, 2.7). Two mechanisms for such a noticeable effect suggest themselves<sup>20)</sup>:

- (1) Iron ions form a deep level in the forbidden band, conduction-band electrons are captured by them, and recombination with valence-band positive holes takes place radiationlessly.
- (2) The excitation energy absorbed in the luminescent centers is transmitted radiationlessly to the iron ions.

Iron ions are harmful to oxysalt phosphors, but to a much smaller extent than they are harmful to zinc sulfide phosphors.

Table 3.1.1 shows examples in which various impurities are added to potassium halophosphate and the powder brightness is measured<sup>21)</sup>. No decrease in powder brightness is seen if 10 ppm Fe, Ni, or Co is added, and only a decrease of about 10% when 100 ppm is added. In the case of Fe, there is good agreement with the calculated value when one simply assumes that part of the 254-nm absorbed light is absorbed by the Fe and goes to waste<sup>22)</sup>. In the case of Ni and Co, however, the powder brightness is much lower than the value calculated under this assumption, so it is thought to be necessary to consider energy transfer from the activator to the impurity ions as in the case of zinc sulfide.

Sometimes, conversely, a minute quantity of additive improves the luminous efficiency. For example, with  $\text{Y}_2\text{O}_3\text{S}:\text{Eu}^{3+}$ , adding  $10^{-4}$  to  $10^{-2}$  atom%  $\text{Tb}^{3+}$  results in an efficiency improvement of up to several percent, as shown in Figure 3.1.6.<sup>23)</sup>  $\text{Pr}^{3+}$  exhibits a roughly similar effect.

The extent of the improved effect caused by  $\text{Tb}^{3+}$  depends on the excitation current density (Figure 3.1.7). That is, the essential effect of  $\text{Tb}^{3+}$  lies in reducing the brightness saturation when the current density is increased. This is thought to be because the  $\text{Tb}^{3+}$  either quenches the sulfur holes that are centers of nonlinear loss causing brightness saturation, or interferes with their operation<sup>23)</sup>.

Another example of a useful minute-quantity additive is cadmium with respect to calcium halophosphate.<sup>24)</sup> In this case, adding 1-2% Cd improves the initial luminous flux of a fluorescent lamp by about 2%. This is attributed to the fact that when the Cd is introduced into the calcium halophosphate, an absorption band arises in the vicinity of 180-190 nm, which absorbs harmful 185-nm ultraviolet radiation and reduces degradation.<sup>25)</sup>